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EFFECTS OF ION BEAM EXCITATION ON CHARGE TRANSFER CROSS SECTION MEASUREMENTS*

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CROSS SECTION MEASUREMENTS*

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Abstract: The charge transfer cross sections for N_2^+ and O_2^+ ions in N_2 have been measured both as a function of ion energy and ion source electron energy. Ion energies were varied between 40 and 1000 eV, and the ion source electron energy was varied between 16 and 24 eV. The resonant N_2^+ in N_2 cross section varied as a function of ion energy in the manner generally reported by other investigators. However the cross section decreased 15 percent in going from 17 to 23 eV in electron energy. This is attributed to metastable ions in the beam which transfer inefficiently. In the O_2^+ in N_2 case, for electron energies below 18 eV, the cross section-vs-ion energy curve was strongly non-resonant, approaching zero cross section below 100 eV. For electron energies above 22 eV, a transfer cross section was quite evident which appeared to have resonance form. The metastable states likely to produce these results are discussed along with their estimated transfer cross sections.

1. Introduction

A great many measurements of charge transfer cross sections involving molecular ions are described in the literature. Although it is expected in these measurements that some of the beam ions will be in long-lived excited states, and, although it is expected that the charge transfer cross sections will be different for the excited ions, it has usually been necessary to ignore the effects of the excitation. It is the purpose of this paper to describe measurements which indicate that the effects of excitation are not only important, but account for the entire cross section in some cases.

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Specifically, the charge transfer cross sections have been measured for N_2^+ in N_2, O_2^+ in N_2, and O_2^+ in O_2 both as a function of the ion energy and the bombarding electron (ion source) energy. The cross section in each case was found to vary significantly with the ion energy and the bombarding electron energy.

2. Procedure

A detailed discussion of the apparatus and procedure has been given elsewhere.[1] A short summary will be presented here. Beams of N_2^+ and O_2^+ ions were produced in an electron bombardment ion source. No magnetic analysis of the beams was used, and this necessitated operation at electron energies where the formation of O^+ and N^+ was not important. Analyses of the ion beam mass spectra were made[2] which showed that the total impurity content was 1% and 2%, respectively, for the N_2^+ and O_2^+ beams.

The ions were electrostatically accelerated to the desired final energies and were then passed through a charge transfer gas cell. The cell consisted of a cylindrical cup and a concentric cylindrical grid within it. The grid was maintained at the potential of the ion beam drift region ("ground") and the "cup potential" difference (Figure 1) was maintained between the grid and cup. The current to the grid and the total current entering the gas cell were measured. Ions scattered with kinetic energy less than the cup potential were collected on the grid, while ions scattered with greater kinetic energy passed through

[1] N. G. Utterback and G. H. Miller, Rev. Sci. Instr. 32, 1101(1961).

[2] N. G. Utterback, Phys. Rev. 129, 219(1963).

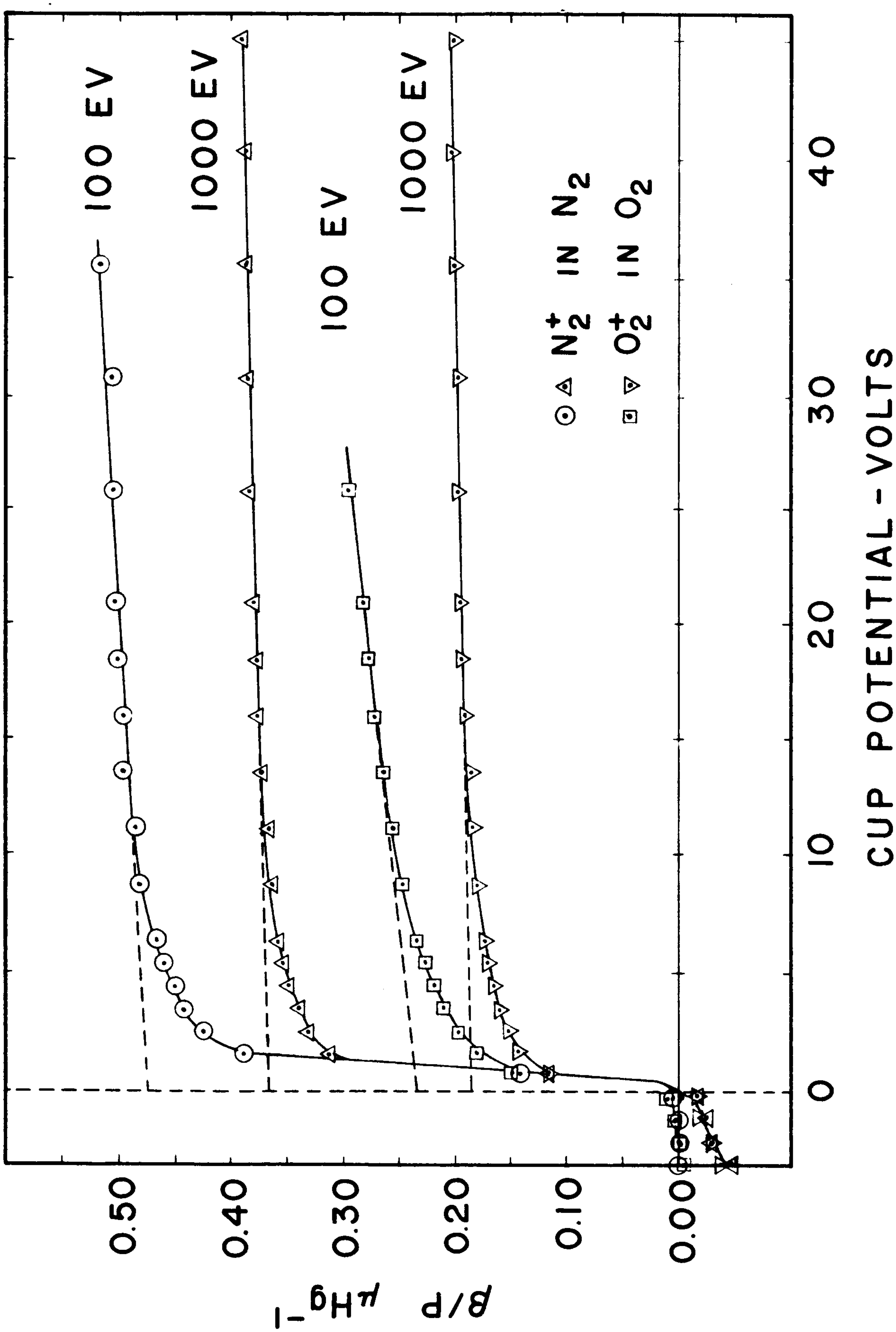

Figure 1. Curves of β/P Versus Cup Potential for N_2^+ in N_2 and O_2^+ in O_2.

the grid to the cup. Thus by varying the cup potential, it was possible to do an energy analysis of the scattered ions. Figure 1 shows such energy analyses, where β is the ratio of grid current to total current entering the cell and P is the gas pressure in the cell. Pressures of the order of 0.1 micron Hg were used.

For a given cup potential in Figure 1, the corresponding β/P values involve the total number of ions having energies up to the cup potential. In order to find the number of ions per energy interval as a function of energy, one must therefore differentiate the curves of Figure 1. Such differentiation shows a large peak of ions having nearly zero kinetic energy, and a smaller background fairly constant with energy. The former corresponds to charge transfer without momentum transfer, and the latter corresponds to scattering with momentum transfer.

The charge transfer cross sections were obtained from the β/P vs. cup potential curves (Figure 1) as follows. The linear portion of each curve was extrapolated back to zero cup potential in order to obtain the β/P value corresponding to ions with very small kinetic energy. For the purposes of this paper, charge transfer will therefore refer to events in which charge was transferred with little transfer of momentum. The charge transfer cross section thus defined is proportional to the extrapolated β/P value, and the proportionality constant may be determined absolutely from physical constants and the gas cell length. Figure 2 shows the charge transfer cross sections for N_2^+ in N_2 and O_2^+ in O_2 obtained in this manner. Results reported in a recent publication[3]

[3] R. F. Stebbings, B. R. Turner, and A. C. H. Smith, J. Chem. Phys. 38, 2277(1963).

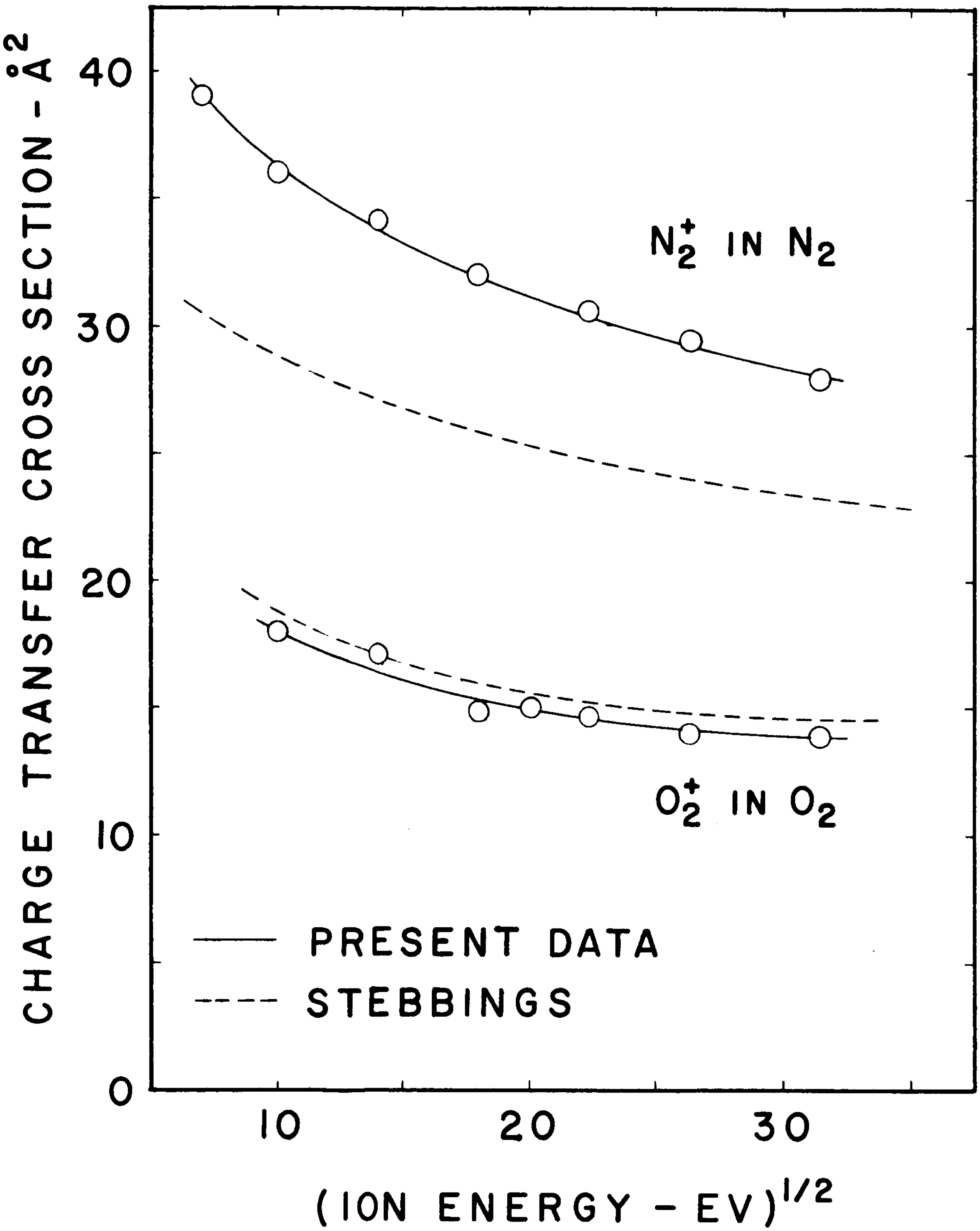

Figure 2. Charge Transfer Cross Sections for N_2^+ in N_2 and O_2^+ in O_2.

are included for comparison.†

The results of varying the bombarding electron energy are shown in Figure 3. The arrows indicate the electron energies at which the curves of Figure 2 were taken. The ion energy for N_2^+ in N_2 was 1000 eV, and for O_2^+ in O_2 it was 100 eV. No direct electron energy calibration was made. Electron energies were determined as follows. For N_2^+ ions, a tungsten filament was used. The potential of the center of the filament was determined and it was assumed that the electrons effective in producing the ions came from that point. One electron volt was added for the electron kinetic energy at the filament. For the O_2^+ ions, a thoria-coated iridium filament was used. Again it was assumed that the electrons came from the center of the filament, but in this case no kinetic energy was added. This method should be accurate to about one electron volt.

3. Discussion of N_2^+ in N_2 and O_2^+ in O_2

The uncertainty in the data presented for this experiment in Figure 2 is estimated to be ±15%. The data of Stebbings, Turner and Smith[3] have about the same uncertainty. The results presented in Figure 2 are therefore quite consistent on an absolute basis. However, it is surprising that the ratio of the N_2^+ in N_2 cross section-to-the O_2^+ in O_2 cross section is so different for the two investigations. Figure 3 indicates that beam ion excitation may explain the discrepancy.

† The results reported here for N_2^+ in N_2 differ from those published earlier.[1] Although the absolute values fall within the previously estimated uncertainties, the change in shape is significant and is due to control of secondary electron effects.

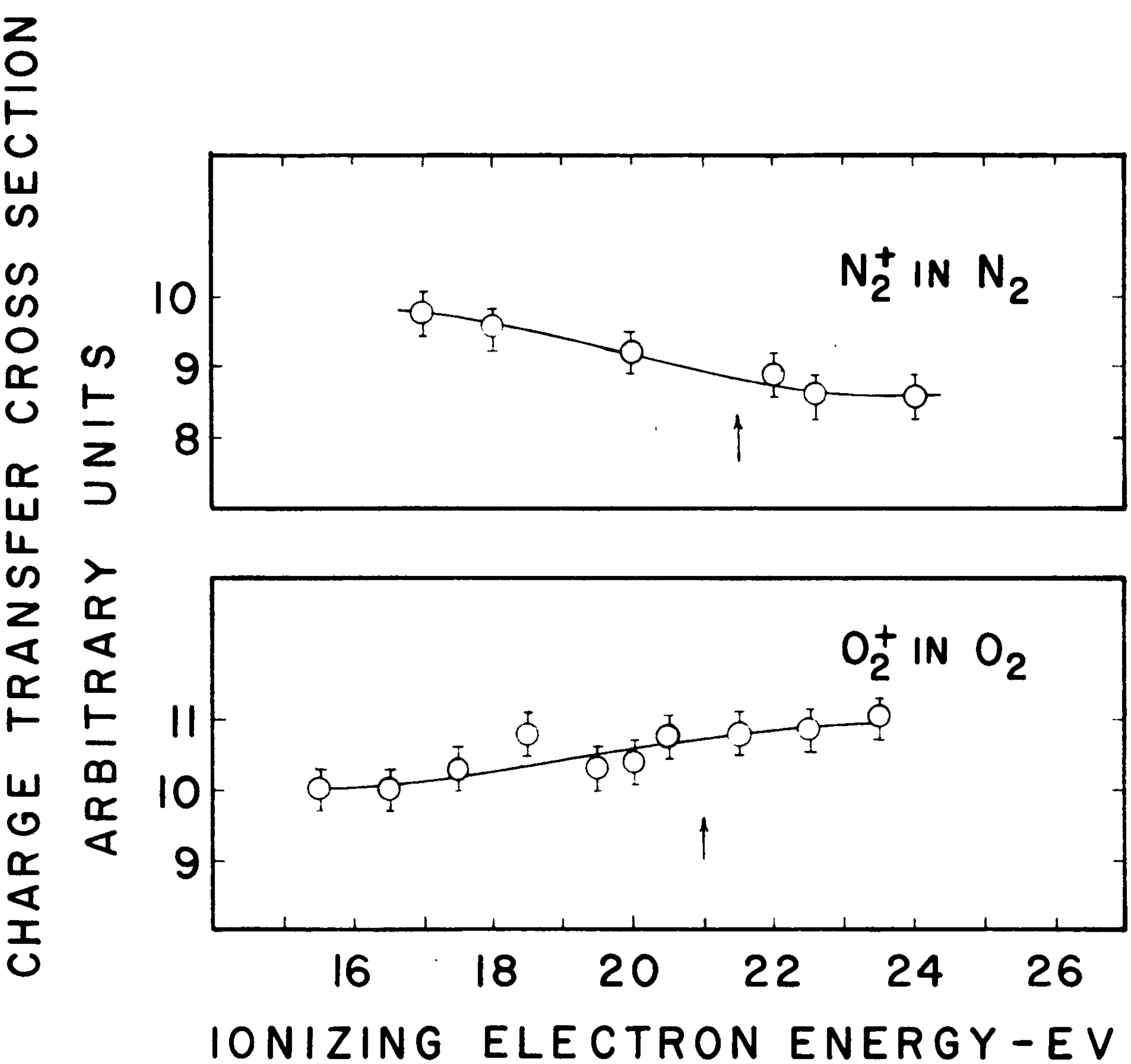

Figure 3. Effect of Varying Ionizing Electron Energy on N_2^+ in N_2 and O_2^+ in O_2.

In the N_2^+ in N_2 case, it appears that excited states in the beam transfer less efficiently than the ground state ions. This might be expected in view of the very large transfer cross section obtained at low electron energies. It is very possible that at higher electron energies (where most other investigations, including reference 3, have been made) the "average" cross section has decreased even further than shown by Figure 3. The $^2\Pi_u$ or the $^2\Sigma_u^+$ state, or both, is involved in the initial decrease. It is not possible to distinguish between these states in this work. (Almost identical results for N_2^+ in N_2 have been obtained independently at Laval University.[4])

In the O_2^+ in O_2 case, the excited ions transfer more efficiently than the ground state ions. This is reasonable because of the relatively low transfer cross section for the ground state ions. In this case it is not as clear whether the "average" charge transfer cross section will rise or fall as more excited states are added at higher electron energies.

4. Results for O_2^+ in N_2

Figure 4 shows the β/P curves for O_2^+ in N_2. These curves correspond to Figure 1 for N_2^+ in N_2 and O_2^+ in O_2 and were obtained in the same manner. The upper curve for each ion energy was taken at an ion source electron energy of 22 eV, and the lower curve was taken at 18 eV electron energy.

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[4] J. W. McGowan, Private Communication.

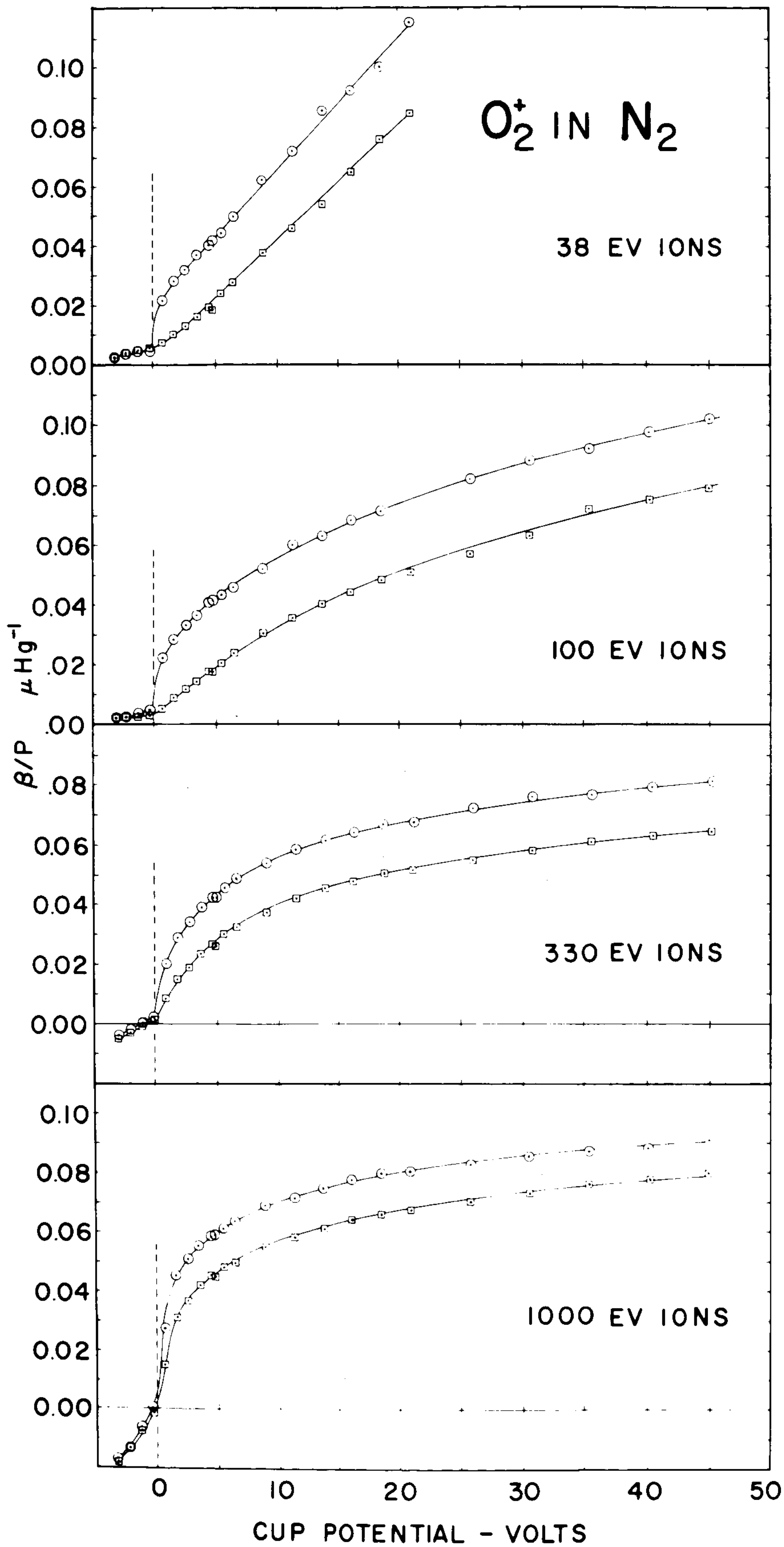

Figure 4. Curves of β/P Versus Cup Potential for O_2^+ in N_2.

The upper curve in Figure 5 shows directly the effect of varying the electron energy while keeping the ion energy constant at 100 eV. This curve is a plot of β/P at a cup potential of 21 volts, as a function of ion source electron energy. The β/P vs. cup potential curves, from which Figure 5 was obtained, were parallel at high cup potentials to the two curves shown in Figure 4 for 100 eV ions.

5. Discussion of O_2^+ in N_2

Three features of Figure 4 are particularly significant here. First, it may be noted that at the lower incident ion energies and for 18 eV electrons (lower curves) for each ion energy there was no peak of very low energy ions corresponding to charge transfer. This is expected since the reaction is endothermic by over three electron volts. The background slope corresponding to ions scattered with momentum transfer has the same order of magnitude as the slopes of the curves in Figure 1 for the other cases. At the higher incident ion energies (with 18 eV electrons), a slow ion peak was present which increased in magnitude with increasing ion energy. Thus the charge transfer cross section for O_2^+ in N_2 showed a strongly non-resonant form so long as the electron energy was low.

Second, for the 22 eV electrons (upper curves for each ion energy) a peak of slow ions was present even at low incident ion energies. The upper and lower curves appear to be identical except for an offset at low cup potential. The difference between the upper and lower curves must be attributed to excited ions which were present in the beam.

Third, the difference between the upper and lower curves for each ion energy decreased as the incident ion energy increased. The charge transfer cross section associated with the excited ions thus had a resonant form.

The negative β/P values appearing for negative cup potentials at high ion energies were due to collection of secondary electrons from the cup when the cup was negative with respect to the grid. These electrons were returned to the cup at positive cup potentials.

Figure 5 shows a comparison of the change in the β/P curves with the known fraction of metastable ions present in the beam, as a function of electron energy. The lower curve of Figure 5 was obtained by extrapolating the linear portions of the appearance potential curve of Frost and McDowell.[5] The contributions of the $^4\Pi_u$ and $^4\Sigma_g^-$ states of the O_2^+ ion were added. The lifetimes were not known, but if the $^4\Sigma_g^-$ state decayed appreciably in the order of 10^{-5} seconds, the $^4\Pi_u$ state was fed by it. The shapes of the curves are similar enough to suggest that the process being observed was charge transfer from the $^4\Pi_u$ state of the O_2^+ to the $^2\Pi_u$ state of the N_2^+. This would necessitate having the $^4\Pi_u$ state in about the sixth vibrational level in order to have energy resonance. This is consistent with Figure 5, in that the observed curve appears to rise somewhat after the appearance of the $^4\Pi_u$ state.

One can not rule out the possibility that the charge transfer is from the $^4\Sigma_g^-$ state (vibrationally excited) of the O_2^+ to the $^2\Sigma_u^+$ state

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[5] D. C. Frost and C. A. McDowell, J. Am. Chem. Soc. 80, 6183(1958).

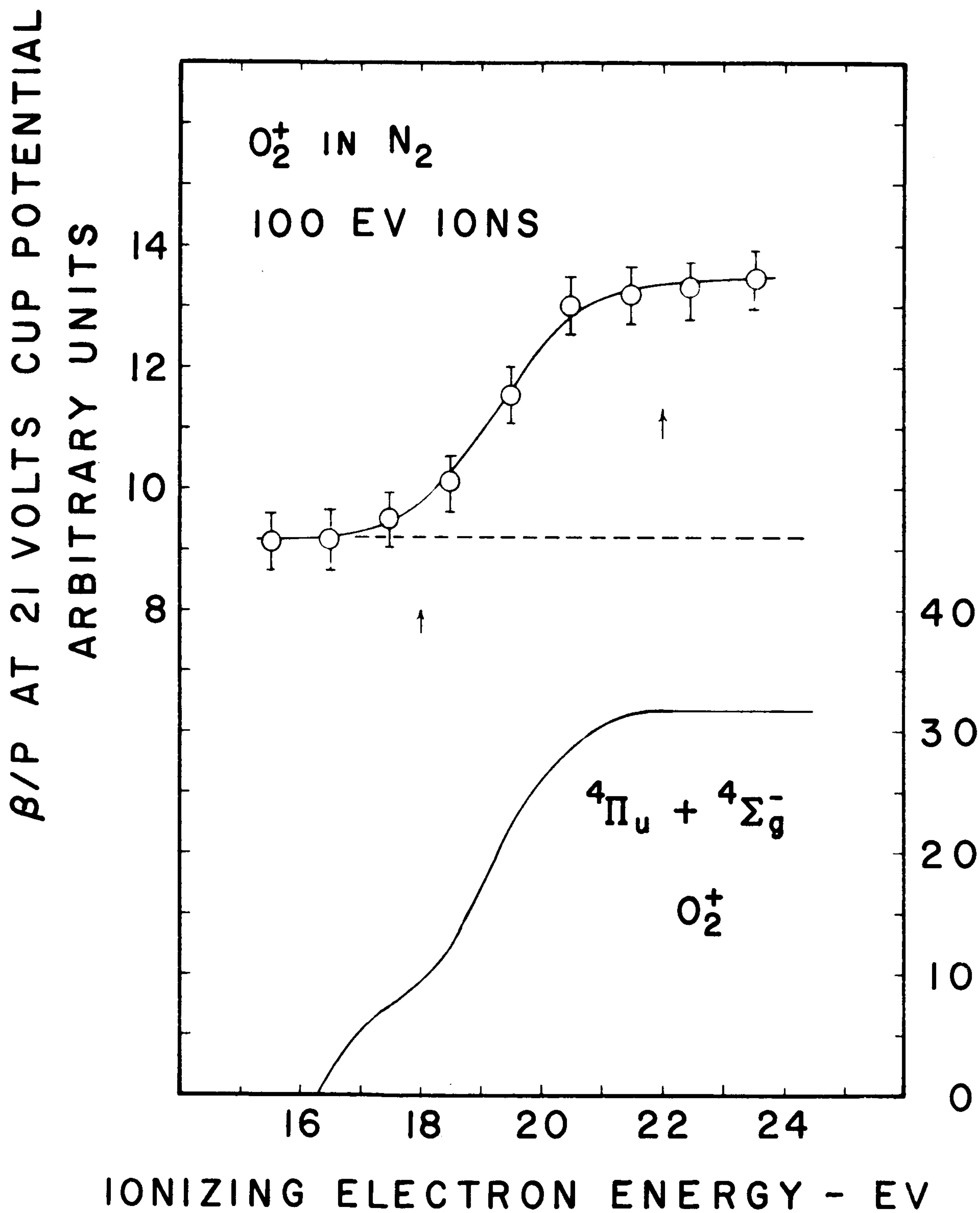

Figure 5. Effect of Varying Ionizing Electron Energy on O_2^+ in N_2.

of the N_2^+ ion, without more knowledge of the lifetime of the $^4\Sigma_g^-$ state.

Figure 6 shows the absolute charge transfer cross section obtained from Figure 4 for the excited ions, assuming that 15% of the beam was in the necessary excited state. The difference between upper and lower curves of Figure 4 was used in obtaining these cross sections. The 15% figure is chosen as a reasonable but arbitrary value. Even if 30% of the beam were effective in the charge transfer, the cross section would only be down by a factor of 2. If the excitation were less than 15%, the cross section would be correspondingly higher. Again, an "average" cross section is probably involved, at least over vibrational levels.

Acknowledgments

The authors wish to thank Dr. R. F. Stebbings and Dr. J. W. McGowan for helpful discussions of this work.

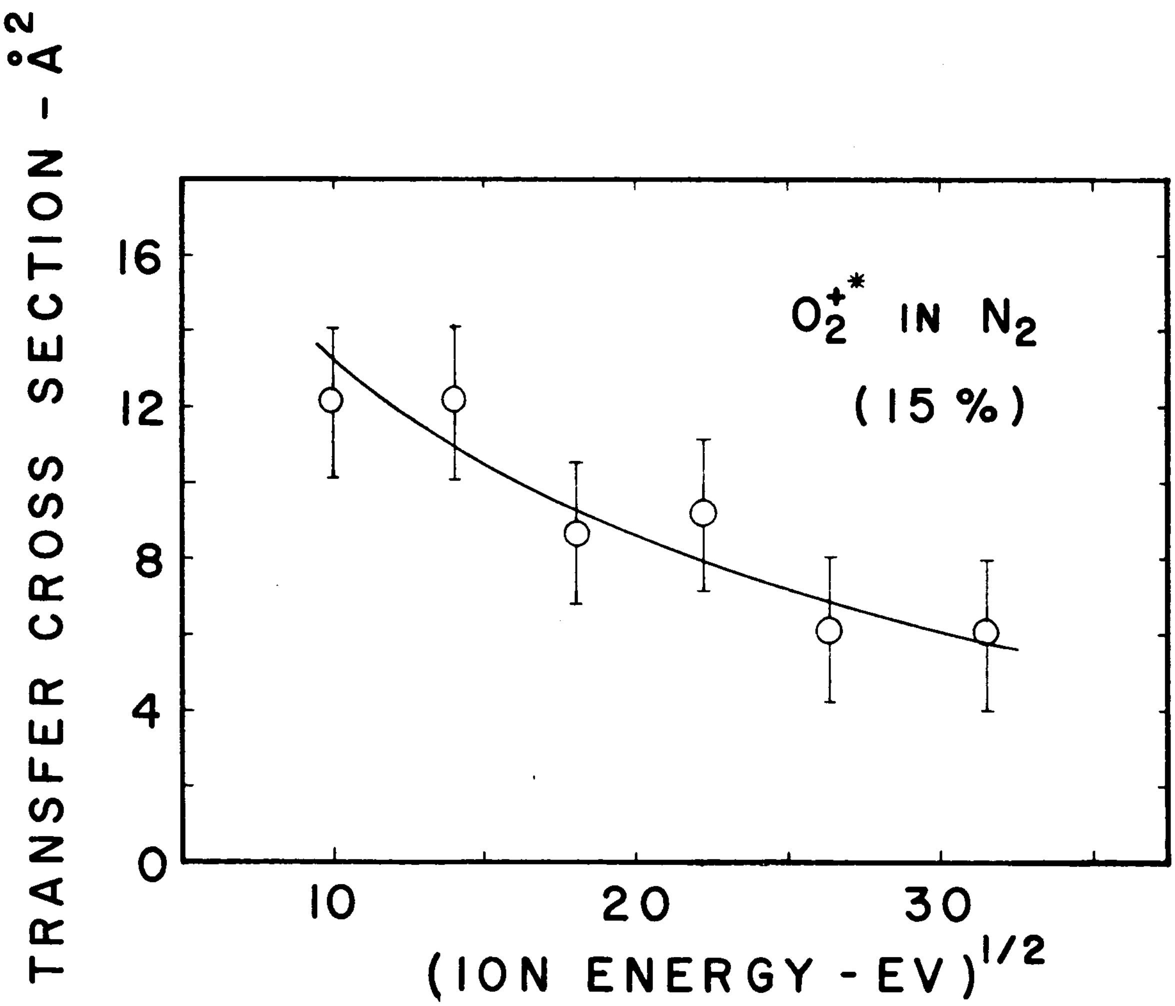

Figure 6. Charge Transfer Cross Section for Excited O_2^+ in N_2.